Journal of Radioanalytical and Nuclear Chemistry, Vol. 253, No. 1 (2002) 115–120

Thermodynamic parameters of Cs^+ sorption on natural clays

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(Received May 10, 2001)

The sorption behavior of Cs^+ on kaolinite, chlorite-illite, and bentonite clays as a function of time, cation concentration, and temperature was studied using the radiotracer method. Sorption data were well represented by Freundlich and Dubinin-Radushkevich type isotherms. Bentonite was found to have the highest sorption capacity and the highest exchange affinity to Cs^+. In all three cases Cs^+ sorption was found to be exothermic with $\Delta H°$ (kJ/mol) –13, –8, –19 and $\Delta S°$ (J/mol·K) –15, 31, and –3 for kaolinite, chlorite-illite, and bentonite, respectively. Negative $\Delta G°$ values were obtained in all cases, indicating the spontaneity of sorption. The magnitudes of $\Delta G°$ suggest that ion exchange is the primary sorption mechanism.

Introduction

Geological repositories are considered as potential sites for radioactive waste disposal for providing protection for the biological environment. Clay minerals have been proposed as suitable backfill materials because of their ability to adsorb cations and thus retard radionuclide migration to the biosphere.[1]

Increasing attention is being paid to sorption studies investigating the interaction between clay minerals and some long-lived radionuclides. Such studies are performed to establish clear understanding of the principal factors that control the sorption process, i.e., the structure of clay minerals, concentration of sorbed cation, sorption time, temperature, pH, particle grain size, and the liquid-solid ratio.

The radionuclide ^{137}Cs is produced in high yield during the fission process and due to its long half-life ($T_{1/2} = 30.17$ y) and its high solubility in the aqueous media, it is a principal radiocontaminant in radioactive wastes. Many studies investigating different aspects of the sorption behavior of this radionuclide on various clay minerals have been carried out.[2–6] In this work the effect of time, cation concentration, and temperature on the uptake of Cs^+ by the clay minerals kaolinite, chlorite-illite, and bentonite was studied.

Experimental

The natural clay minerals used were obtained from the Turkish General Directorate of Mineral Research and Exploration (MTA). They originated from Sindirgi, Afyon, and Giresun regions of Turkey. Both Sindirgi and Afyon are located in the western part of Anatolia, whereas Giresun is situated in the north eastern Anatolia, on the Black Sea coast. The X-ray diffraction analysis showed that Sindirgi clay consisted of kaolinite and some quartz, Afyon clay contained chlorite-illite mixed clay together with some calcite and quartz, and Giresun clay consisted primarily of bentonite (montmorillonite) and some quartz and feldspar. The X-ray diffraction spectra of the clays used are given in Fig. 1. The unfractionated particle size of kaolinite, chlorite-illite, and bentonite used were all <38 μm.

The batch method was used, and prior to the sorption experiments pretreatment of the clay samples was carried out. This pretreatment step was intended to mimic the equilibrium existing between the natural clays and groundwater. Aliquots of 30 mg of the clay were introduced into pre-weighed tubes, and 3 ml of Bilkent tapwater, as substitute for groundwater, were added into each tube which were then shaken for 4 days with a lateral shaker at 125 rpm. The cation composition of Bilkent tapwater was determined by collecting different samples over a period of three months and analysing them by FAAS. The average concentrations (meq/ml) of Na^+, K^+, Mg^{2+}, and Ca^{2+} in Bilkent tapwater were $3.92 \cdot 10^{-4}$, $1.04 \cdot 10^{-4}$, $4.30 \cdot 10^{-4}$, and $3.24 \cdot 10^{-4}$, respectively. Samples were then centrifuged at 6000 rpm for 30 minutes and the liquid phases were discarded. Each tube was then weighed to determine the remaining small amount of water (ΔW_{pt}).

Effect of the contact time

To each of the 30 mg pretreated clay samples, 3 ml of solution containing $1 \cdot 10^{-3}$ meq/ml of Cs^+ with appropriate amount of ^{137}Cs radiotracer was added. The initial activity of cesium solutions was $2.77 \cdot 10^6$ Bq using the prominent γ-ray of 662 keV. The samples were shaken at room temperature for periods ranging from one hour to seven days, then centrifuged and 2 ml portions of the liquid phases were counted, using a 35 cm^3 calibrated HPGe detector connected to a multichannel analyzer. Duplicate samples were used in each measurement.

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0236–5731/2002/USD 17.00

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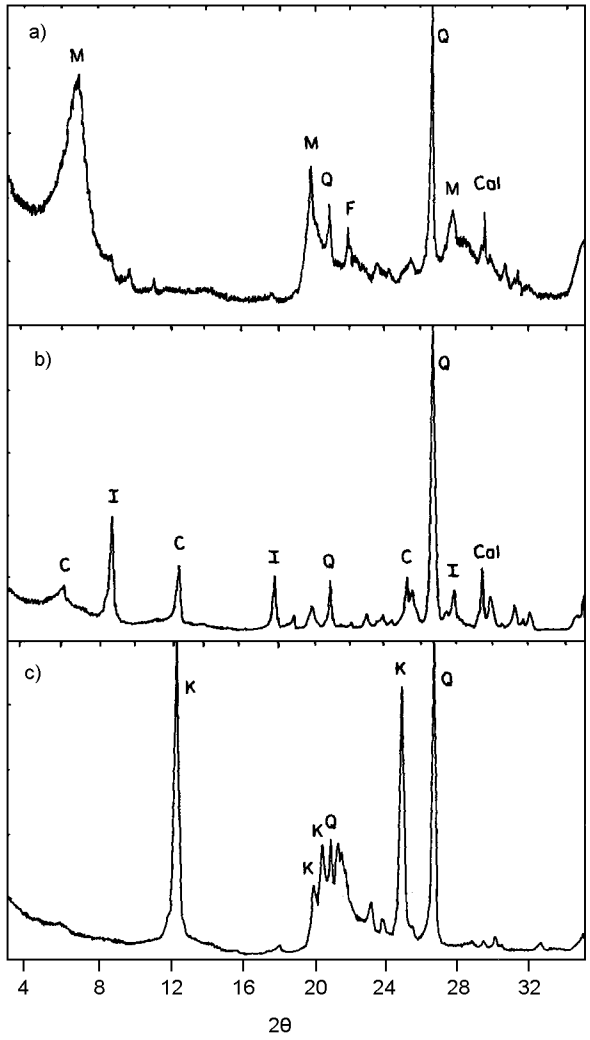

Fig. 1. The XRD spectra of natural clay minerals used in this study; bentonite (a), chlorite-illite (b), and kaolinite (c); K – kaolinite, C – chlorite, I – illite, M – montmorillonite, Cal – calcite, Q – quartz, F – feldspars

Effect of the loading and temperature

Loading studies were carried out to investigate the effect of Cs^+ concentration on sorption at different temperatures. The experiments were performed at the initial concentrations of $1\cdot10^{-3}$, $1\cdot10^{-4}$, $1\cdot10^{-5}$, and $1\cdot10^{-6}$ (meq/ml) at four different temperatures; 30, 40, 50 and 60 °C. Three ml of Cs^+ solution containing an appropriate amount of ^{137}Cs was added to each sample tube containing 30 mg of the particular clay at the desired temperature. Duplicate samples were shaken for two days, centrifuged and 2 ml portions of the liquid phase were counted. Shaking was done in a temperature-controlled environment using a Nuve ST 402 water bath shaker equipped with a microprocessor thermostat.

The uncertainties associated with the measurements stemmed principally from those of activity. Other minor error sources were those originating from weight and volume measurements. Based on error sources, the percentage error in the R_d values was calculated to be less than ±5%, depending on the measured activities.

Mathematical relations

The distribution ratio, R_d

The experimental data in sorption are expressed in terms of the distribution ratio, R_d, defined as the ratio of sorbate concentration on solid phase to its concentration in liquid phase. R_d can be expressed in terms of activity by:[2]

$$R_d = \frac{VA^{\circ} - (V + \Delta W_{pt})A_l}{A_l W_s} \quad (1)$$

where $A°$ is the initial count rate of solution added for sorption (cps)/ml, A_l is the count rate of solution after sorption (cps)/ml, V is the volume of the solution (ml), W_s is the weight of the solid material (g), ΔW_{pt} is the amount of liquid remaining in the tube after pretreatment, before sorption.

Freundlich isotherm

It is the most widely applicable non-linear model for describing the dependence of sorption on adsorbate concentration. This model allows for several kinds of sorption sites on the solid and represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces. The general expression of Freundlich isotherm is given as:

$$[C]_s = k\,[C]_l^n \quad (2)$$

where $[C]_s$ is the amount of ionic species adsorbed on the solid matrix at equilibrium (meq/g), $[C]_l$ is the concentration of the cation in solution at equilibrium (meq/ml), k and n are Freundlich constants.

This expression can be linearized as:

$$\log [C]_s = \log k + n \log [C]_l \quad (3)$$

Plotting $\log[C]_s$ vs. $\log[C]_l$ yields n as the slope and $\log k$ as the intercept.

Equation (2) can be rearranged to give the distribution ratio, R_d, which represents the concentration of the sorbate on the solid phase to that on the liquid phase, in the following manner:

$$R_d = k\,[C]_l^{n-1} \quad (4)$$

Dubinin-Radushkevich (D-R) isotherm

The D-R isotherm model is applicable at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. It can be represented by the general expression:

$$[C]_s = C_m \exp{-(K\varepsilon^2)} \quad (5)$$

where ε is the Polanyi potential, given as $RT\ln(1+1/[C]_l)$, R is the ideal gas constant (8.3145 J/mol·K), T is the absolute temperature (K), K is a constant related to the energy of sorption, C_m is the sorption capacity of adsorbent per unit weight (meq/g).

The linear form of the equation above may be obtained by rearranging it:

$$\ln [C]_s = \ln C_m - K\varepsilon^2 \quad (6)$$

If $\ln [C]_s$ is plotted against ε^2, K and $\ln C_m$ will be obtained from the slope and the intercept, respectively. The value of K $(\text{mol/kJ})^2$ is related to the adsorption mean free energy, E (kJ/mol), defined as the free energy change required to transfer one mole of ions from the infinity in the solution to the solid surface.[7] The relation is given as:

$$E = (-2K)^{-0.5} \quad (7)$$

Thermodynamic relations

In a batch adsorption process, the adsorption reaction can be written as:

$$C_l + \underline{S}_{(s)} \Leftrightarrow C_s \quad (8)$$

where C_l stands for the solute particle s in solution, $\underline{S}$ for the sorption sites on the surface of the adsorbent and C_s for the solute particles adsorbed on the adsorbent. The equilibrium constant for the reaction above can be written in terms of the activities as:

$$K = \frac{a_{C_s}}{a_{\underline{s}} \cdot a_{C_1}} \quad (9)$$

The activity of the solid phase can be taken as unity at the reference state, then the above expression can be written in terms of the concentrations and the activity coefficients γ as:

$$K = \frac{[C]_s}{[C]_1} \cdot \frac{\gamma_{C_s}}{\gamma_{C_1}} \quad (10)$$

For dilute solutions the activity coefficients can be taken as unity, so that the equilibrium constant becomes equivalent to the distribution coefficient R_d, defined as the ratio of the solute concentration on the solid phase to that on the liquid phase.

In line with the above derivation, the distribution coefficient may be related to the change in Gibbs free energy, ΔG, by:

$$\Delta G = \Delta G° + RT\ln R_d \quad (11)$$

where $\Delta G°$ is the standard Gibbs free energy change, R is the ideal gas constant, and T is the absolute temperature.

At equilibrium no change in Gibbs free energy occurs and the above equation reduces to:

$$\Delta G° = -RT\ln R_d \quad (12)$$

So, using Eq. (12), it is possible to determine $\Delta G°$ of sorption directly from the R_d values at different temperatures.

Gibbs free energy change can also be written in terms of enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, as given below:

$$\Delta G° = \Delta H° - T\Delta S° \quad (13)$$

Combining Eqs (12) and (13) the following expression results:

$$\ln R_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (14)$$

By plotting $\ln R_d$ versus $1/T$, it is possible to determine the value of $\Delta H°$ of sorption from the slope and $\Delta S°$ of sorption from the intercept of the linear fits.

Results and discussion

The variation of R_d values for the sorption of Cs^+ on kaolinite, chlorite-illite, and bentonite as a function of sorption time indicates a fast sorption process. This is more pronounced at the early sorption stages during the first few hours of contact time. A somewhat slower process follows where some desorption occurs leading finally to equilibrium in about two days of contact.

Loading experiments were carried out to investigate the effect of initial cation concentration on sorption. R_d values of Cs^+ sorption on the three clays at various initial cation concentrations and temperatures are given in Table 1. It is interesting to note that at higher loading, the highest R_d values were obtained for bentonite, whereas at lower loading, chlorite-illite mixed clay had the highest R_d values. This might suggest the existence of energetically more favourable sites in chlorite-illite clay which have limited sorption capacity and are thus more efficient in Cs^+ sorption from dilute solutions. The existence of this type of sites in illite was reported by other studies.[6,8]

The loading curves were constructed by plotting R_d values against $\log [C]_s$, as illustrated in Fig. 2 for kaolinite, chlorite-illite, and bentonite at 30 °C. The curves in the figure were drawn to guide the eye.

Table 1. The distribution ratio, R_d (in ml/g), values of Cs^+ sorption on kaolinite, chlorite-illite, and bentonite at various temperatures and initial concentrations, [*C*]° (meq/ml)

Clay	[*C*]°, meq/ml	R_d at different temperatures			
		303 K	313 K	323 K	333 K
Kaolinite	$1\cdot10^{-6}$	58	56	53	47
	$1\cdot10^{-5}$	48	44	36	30
	$1\cdot10^{-4}$	36	33	26	22
	$1\cdot10^{-3}$	28	22	17	15
Chlorite-illite	$1\cdot10^{-6}$	2581	2132	2207	1966
	$1\cdot10^{-5}$	1743	1594	1384	1039
	$1\cdot10^{-4}$	1156	978	933	883
	$1\cdot10^{-3}$	174	157	154	146
Bentonite	$1\cdot10^{-6}$	1291	1273	831	825
	$1\cdot10^{-5}$	1223	1179	697	697
	$1\cdot10^{-4}$	985	946	630	619
	$1\cdot10^{-3}$	919	598	396	373

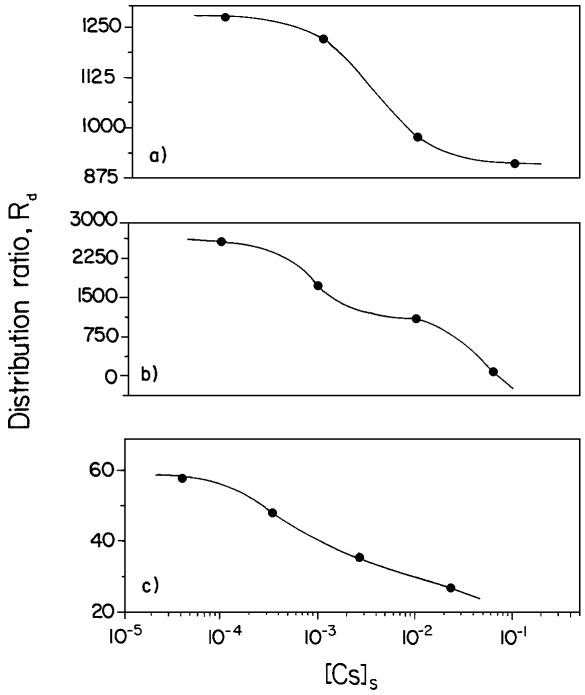

Fig. 2. Loading curves of Cs^+ sorption on clays at $T = 30$ °C

According to those curves, Cs^+ sorption on bentonite shows a characteristic inverse S shape indicating that the sorption occurs on two sites: one at high loading, the other at low loading within the concentration range of the experiments. The chlorite-illite curve implies that two or more sorption sites exist with large differences in R_d values. The loading curve of kaolinite suggests a single sorption site. Both kaolinite and chlorite-illite clays seem to approach saturation at higher loading.

Freundlich isotherm

The results of Freundlich isotherm fits to the sorption data are given in Table 2. Typical isotherm plots at 30 °C are shown in Fig. 3a. The magnitude of the constant *k* provides quantitative information on the relative sorption affinity towards the sorbed cation and the magnitude of constant *n* is an indicator of linearity of sorption. The deviation of *n* from unity indicates a non-linear sorption that takes place on heterogeneous surfaces.[9] The nonlinear behavior implies that the sorption energy barrier increases exponentially as the fraction of filled sites on the clay increases, hence an increase in the initial concentration leads to a decrease in the R_d values. According to the *n* values in Table 2, the nonlinearity is highest in the case of chlorite-illite. The magnitudes of *k* indicate that bentonite has the highest sorption affinity towards Cs^+ ion. Increase of temperature has no pronounced effect on *n*, but the *k* values of bentonite and kaolinite decrease appreciably. This suggests that the nonlinearity of sorption is retained at higher temperatures. The decrease in sorption affinity as temperature is increased stems from the exothermic sorption behavior as discussed later.

The Freundlich isotherm model provided the best description of the experimental data. Hence, empirical equations relating R_d to the equilibrium concentration in the liquid phase were developed utilizing the Freundlich isotherm parameters, *n* and *k*. If the variation of *k* and/or *n* as a function of temperature is incorporated within Eq. (4), it would be possible to predict R_d values for various loading and temperature conditions.

Table 2. Freundlich isotherm constants, k and n, obtained from the least square fits to the sorption data

Temperature, K	Kaolinite		Chlorite-illite		Bentonite	
	n	k	n	k	n	k
303	0.90	13.4	0.71	23.1	0.95	616.6
313	0.87	9.1	0.71	22.5	0.90	281.8
323	0.86	7.1	0.71	21.6	0.91	208.9
333	0.84	4.9	0.72	22.2	0.90	173.8

The linear correlation coefficients were all greater than 0.998.

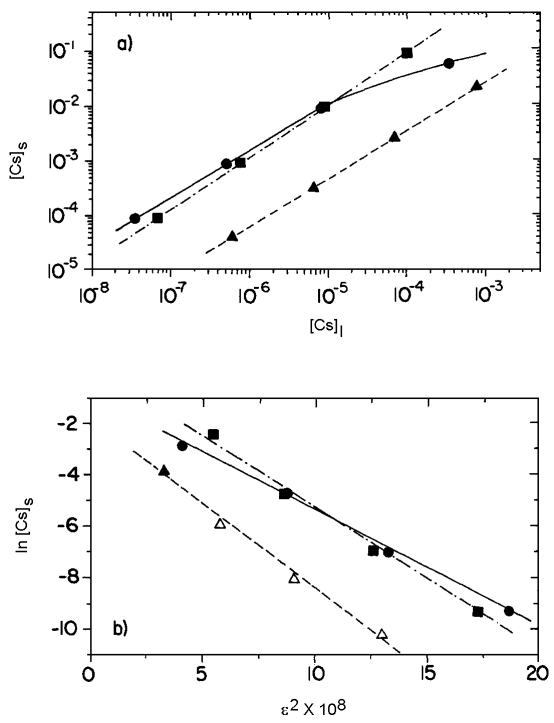

Fig. 3. Freundlich isotherms of Cs^+ sorption on kaolinite, chlorite-illite, and bentonite at T = 30 °C (a); ■ kaolinite, ● chlorite-illite, ▲ bentonite. Dubinin-Radushkevich isotherms of Cs^+ sorption on kaolinite, chlorite-illite, and bentonite at T = 30 °C (b); ■ kaolinite, ● chlorite-illite, ▲ bentonite

Table 3. Values of a, b, and $\breve{n}$ in the empirical relation $R_d = (a+bT)[C]_l^{\breve{n}-1}$ for the sorption of Cs^+ on kaolinite, chlorite-illite, and bentonite

Clay	a	b	$\breve{n}$
Kaolinite	96.1	–0.28	0.87
Chlorite-illite	22.4	0.0	0.71
Bentonite	1965.9	–5.40	0.92

The values of n and k are given in Table 2. It is seen that while the values of n are temperature independent, those of k vary with temperature. As a result the n values are expressed in terms of their average throughout the entire temperature range. The k values, on the other hand, are plotted as a function of temperature and expressed a linear function. Based on this, R_d can be written by the general equation:

$$R_d = (a + bT)[C]_l^{\breve{n}-1} \qquad (15)$$

where $(a+bT)$ corresponds to k, a and b are constants, T is the temperature (K), and $\breve{n}$ is the average of n values obtained from Freundlich isotherm fits.

The values of a, b, and $\breve{n}$ for sorption of Cs^+ on kaolinite, chlorite-illite, and bentonite are given in Table 3. The significance of Eq. (15) is the incorporation of the entire concentration and temperature ranges into the R_d values. Consequently, they can be used in the prediction of the loading curves and sorption isotherms at various temperatures in addition to Arrhenius plots used in the calculations of the thermodynamic parameters.

Dubinin-Radushkevich isotherm

The D-R isotherm parameters K, C_m and E obtained from fitting the experimental data to Eqs (6) and (7) are given in Table 4. Typical plots at 30 °C are given in Fig. 3b. The sorption capacity order obtained from C_m values is bentonite > chlorite-illite > kaolinite. The mean free energy of sorption, E, is in all cases in the range corresponding to the ion-exchange type of adsorption.[10]

Thermodynamic results

The values of $\Delta H°$ and $\Delta S°$ of Cs^+ sorption were obtained by fitting the experimental data to Eq. (12) as shown in Fig. 4. $\Delta G°$ values were calculated using Eq. (14). The results are given in Table 5. Since no appreciable variation was observed, the results were averaged over the concentration and temperature ranges. The negative $\Delta H°$ values show that sorption of Cs^+ on all clays in this work is exothermic in nature. The exothermic behavior of Cs^+ was reported on other solids.[4,11,12] The negative $\Delta S°$ values corresponding to sorption on kaolinite and bentonite indicate a stable arrangement of Cs^+ on the clay surface. The positive $\Delta S°$ value in the case of Cs^+ sorption on chlorite-illite is questionable in terms of stability but is favored in terms of the spontaneity of sorption. The negative $\Delta G°$ values in all cases indicate that the Cs^+ sorption is spontaneous.

Table 4. The D-R isotherm constants, K (in mol/kJ)^2 and C_m (in meq/100g) obtained from the least square fits to the sorption data and the mean free energy, E (kJ/mol) values obtained from K values

Temperature, K	Cs-kaolinite			Cs-chlorite-illite			Cs-bentonite		
	K	C_m	E	K	C_m	E	K	C_m	E
303	0.0065	13.9	8.8	0.0045	37.9	10.5	0.0057	158.1	9.4
313	0.0059	11.0	9.2	0.0043	38.3	10.8	0.0052	116.0	9.8
323	0.0055	9.4	9.5	0.0040	36.8	11.2	0.0051	94.6	9.9
333	0.0051	6.6	9.9	0.0038	35.7	11.5	0.0048	91.6	10.2

The linear correlation coefficients were all greater than 0.996.

Table 5. The enthalpy change, $\Delta H°$, entropy change, $\Delta S°$, and Gibbs free energy change, $\Delta G°$ obtained from the data of Cs^+ sorption on kaolinite, chlorite-illite, and bentonite

	Kaolinite	Chlorite-illite	Bentonite
$\Delta H°$, kJ/mol	–13 ± 4	–8 ± 2	–19 ± 4
$\Delta S°$, J/mol·K	–15 ± 8	31 ± 10	–3 ± 1
$\Delta G°$, kJ/mol	–9 ± 1	–18 ± 3	–18 ± 1

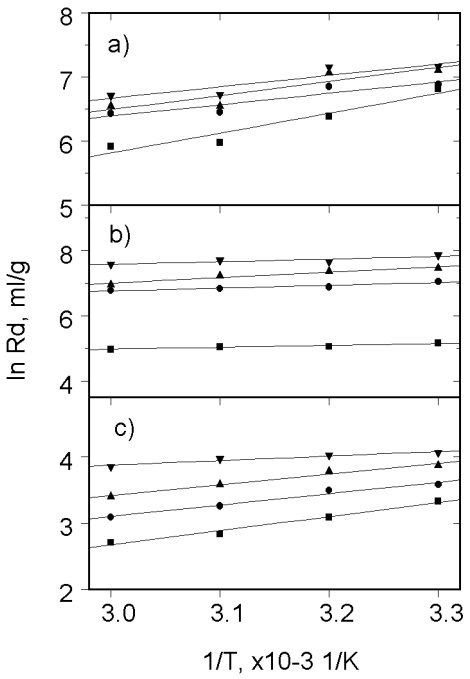

Fig. 4. $\ln R_d$ vs. $1/T$ plots in the sorption of Cs^+ on bentonite (a), chlorite-illite (b), and kaolinite (c) at different initial concentrations: ■ $1.0\cdot10^{-3}$ meq/ml, ● $1.0\cdot10^{-4}$ meq/ml, ▲ $1.0\cdot10^{-5}$ meq/ml, ▼ $1.0\cdot10^{-6}$ meq/ml

It must be noted here that the difference in sign between E obtained from the D-R isotherms and $\Delta G°$ values arises from the definition of E. The magnitudes of both indicate an ion exchange type sorption mechanism.

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